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Hydrolysis of epoxides and aziridines catalyzed by polymer-supported quarternary ammonium bisulfate

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Abstract

Macroporous resin (D201)-supported quarternary ammonium bisulfate (D201-HSO_4) was prepared and effectively used in catalyzing the hydrolysis of epoxides or aziridines under mild and non-metal conditions to give the corresponding 1,2-diols and β-amino alcohols in high yields. The catalyst was facilely prepared and recyclable.

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Anion-exchange resins have been widely used as catalysts in organic synthesis [1]. Conventional strongly basic anion-exchange resins or those which carry other functional groups were used as phase-transfer catalysts in preparations of cyanide or ether. Sometimes, they are used as substitute for small basic molecule to catalyze aldol condensation, addition, rearrangement, *etc.* [2,3]. Simple separation and reusability are the principal advantages of polymer-supported catalysts.

1,2-Diols and β-amino alcohols are important intermediates in organic synthesis. They are usually prepared by ring-opening of epoxides and aziridines in the presence of either Lewis acids or strong bases [4–8]. Recently *n*-Bu_4NHSO_4 was found to be an efficient catalyst for the hydrolysis of aziridines and epoxides under mild condition [9], but the preparation of *n*-Bu_4NHSO_4 is tedious. Polymer-supported quarternary ammonium bisulfates could be facilely prepared from anion-exchangers, however there are few reports about the effects of them in the ring-opening reactions. In this paper, we would like to describe an efficient method for the ring-opening reaction of epoxides **1** or *N*-substituted aziridines **2** in water catalyzed by polymer-supported quarternary ammonium bisulfate (D201-HSO_4), which was facilely prepared and recyclable, to obtain 1,2-diols **3** or β-amino alcohols **4** (or **5**) in moderate to excellent yields (Scheme 1).

A macroporous quarternary ammonium anion-exchange resin D201 × 7 (chloride form, with 50–60% water content and 20–50 mesh, 1.1 mmol Cl^-/mL wet resin), available from Shandong Lukang Record Pharmaceuticals Limited Company, was used as support. Preparation of D201-HSO_4: resin D201 in chloride form (58 g) was pretreated with 300 mL of 2 mol/L HCl, and then washed with demonized water till the pH value of the fluent was 3–4. The resin

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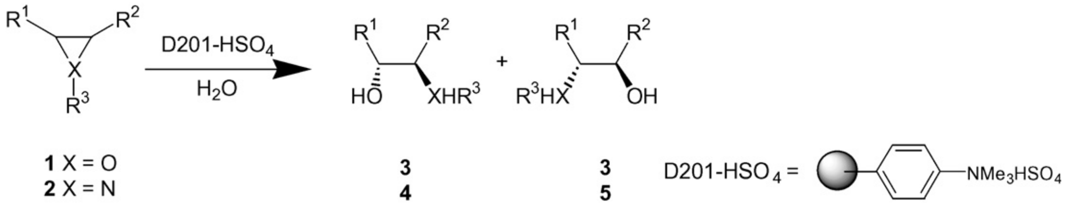

Scheme 1.

Table 1
The results of hydrolysis of **1** and **2** catalyzed by the resin D201-HSO_4[a]

Entry	Sub. X	*R*¹ and *R*²	*R*³	Solvent	*T* (°C)	Product	Yield (%)	Reference
1	**1a**, O	Ph, H	None	H_2O	25	**3a**	96	[9]
2	**1b**, O	$-(CH_2)_4-$	None	H_2O	25	**3b**	99	[9]
3	**1c**, O	$ClCH_2$, H	None	H_2O	50	**3c**	68	[9]
4	**1d**, O	*n*-Bu, H	None	H_2O	25	**3d**	72	[9]
5	**1e**, O	$CH_2 = CH(CH_2)_4$, H	None	H_2O	25	**3e**	73	[9]
6	**2a**, N	$-(CH_2)_4-$	Ts	H_2O/CH_3CN (1:1)	60	**4a**	97	[9]
7	**2b**, N	Ph, H	Ts	H_2O/CH_3CN (1:1)	60	**4b**, **5b**	95(>95:5)[b]	[9]
8	**2d**, N	$-CH_2CH = CHCH_2-$	Ts	H_2O/CH_3CN (1:1)	60	**4d**	96	[10]
9	**2e**, N	Bn, H	Ts	H_2O/CH_3CN (1:1)	60	**4e, 5e**	86(<5:95)[b]	[11]
10	**2f**, N	$-(CH_2)_5$-	Ts	H_2O/CH_3CN (1:1)	60	**4f**	No Reac.	[9]

[a] All the products were identified by spectroscopy methods and by comparison with the authentic sample.
[b] The ratio of isomers was determined by ^1H NMR.

exchanged with 300 mL of 2 mol/L Noah through chromatographic column giving the resin in hydroxide form, which was washed with demonized water till the fluent was neutral. The resin was reacted with 2 mol/L H_2SO_4, thoroughly washed with demonized water and D201-HSO_4 was obtained. It was directly used without further torrefaction.

General procedure of ring-opening reaction: to a solution of epoxide **1** or aziridine **2** (2.0 mmol) in 2.0 mL of solvent was added the resin D201-HSO_4 (0.5 mL). The mixture was stirred at a specified temperature for 24–72 h. After **1** (or **2**) was completely consumed (monitored by TLC), the mixture was filtrated, and the resin was washed with ethanol and Et_2O in sequence. The filtrate was then concentrated and 2.0 mL of H_2O was added to the residue. The mixture was extracted with Et_2O, dried over anhydrous $MgSO_4$, filtered and vaporized. The crude product was purified by flash column chromatography. All the products are known and their physical spectral data were identical to those reported in the literature (Table 1).

Epoxide **1a** and aziridine **2a** were used to investigate the reaction conditions. **1a** could be smoothly hydrolyzed in water giving diol **3a** in the presence of D201-HSO_4 at room temperature. However, when organic solvent (such as THF, CH_3CN) was absent, **2a** could not react with water to give **4a** or **5a**. In order to enhance the solubility of **2a** in the reaction mixture, CH_3CN was added as cosolvent ($H_2O/CH_3CN = 1:1$). In addition, aziridines **2a** should be hydrolyzed at relatively high temperature (60 °C).

Various epoxides **1** and aziridines **2** were used to test the catalytic ability of this catalyst under the corresponding conditions (Table 1). It can be seen from Table 1 that various epoxides or aziridines could be hydrolyzed to give 1,2-diol or β-amino alcohols in moderate to excellent yields. Most of epoxides were hydrolyzed at 25 °C, but 1,2-epoxy-3-chloropropane **1c** (Table 1, entry 3) should react at 50 °C giving **3c** in moderate yield.

In most cases, aziridines were hydrolyzed to give rise to the corresponding β-amino alcohols in high yields, but aziridine **2f** bearing seven-membered ring were not reacted with water even at 60 °C (Table 1, entry 11) though it could be hydrolyzed into **4f** in the presence of *n*-Bu_4NHSO_4. This may reflect the difference between catalysts D201-HSO_4 and *n*-Bu_4NHSO_4. Acyclic terminal aziridines **2b** and **2e** gave information about the regiochemistry of the reaction. **4b** was the only product of **2b** whose hydroxyl group linked phenyl-substituted carbon, as expected for a charge-controlled ring-opening process (entry 7, Table 1) [12]. However, for the alkyl-substituted aziridine **2e**, its products **5e** was resulted from the attack of H_2O to **2e** from the side with less subsituents, which reflected the influence of hindrance on the ring-opening pathways for this type of aziridine (entry 9, Table 1).

To investigate the reusability of catalyst D201-HSO_4 in the reaction of **1a** with water, the recovered catalyst was reused two times, and similar yields of **3a** were obtained (yield: fresh D201-HSO_4: 96%, cycle 1: 94%, cycle 2: 94% yield). The results indicated that the polymer-supported catalyst can be reused without loss of activity in this experimental condition.

In conclusion, macroporous resin D201-HSO_4 was an efficient and recyclable catalyst for the hydrolysis of epoxides or aziridines under non-metal conditions. The reactions provide 1,2-diols and β-amino alcohols in high to excellent yields in a simple and convenient way, which offers a new promise of economical process.

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